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| FORM PTO-1390 (REV. 12-2001) | | U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE | | ATTORNEY'S DOCKET NUMBER <div style="text-align: center; font-size: 1.2em;">20291</div> | |
| TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371 | | | | U.S. APPLICATION NO. (If known, see 37 CFR 1.5 <div style="text-align: center; font-size: 1.5em; font-weight: bold;">10/031220</div> | |
| INTERNATIONAL APPLICATION NO. <div style="text-align: center;">PCT/CN00/00196</div> | | INTERNATIONAL FILING DATE <div style="text-align: center;">13 July 2000</div> | | PRIORITY DATE CLAIMED <div style="text-align: center;">16 July 1999</div> | |
| TITLE OF INVENTION <div style="text-align: center; font-weight: bold;">A PROCESS FOR PRODUCING GASOLINE AND DIESEL FROM WASTE PLASTICS</div> | | | | | |
| APPLICANT(S) FOR DO/EO/US <div style="text-align: center;">ZHOU, Jifu</div> | | | AND/OR HEAVY OIL | | |
| Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information: | | | | | |
| 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. | | | | | |
| 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. | | | | | |
| 3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below. | | | | | |
| 4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). | | | | | |
| 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) | | | | | |
| a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). | | | | | |
| b. <input type="checkbox"/> has been communicated by the International Bureau. | | | | | |
| c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). | | | | | |
| 6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). | | | | | |
| a. <input checked="" type="checkbox"/> is attached hereto. | | | | | |
| b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). | | | | | |
| 7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) | | | | | |
| a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). | | | | | |
| b. <input type="checkbox"/> have been communicated by the International Bureau. | | | | | |
| c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. | | | | | |
| d. <input type="checkbox"/> have not been made and will not be made. | | | | | |
| 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)). | | | | | |
| 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). | | | | | |
| 10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). | | | | | |
| Items 11 to 20 below concern document(s) or information included: | | | | | |
| 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. | | | | | |
| 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. | | | | | |
| 13. <input type="checkbox"/> A FIRST preliminary amendment. | | | | | |
| 14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. | | | | | |
| 15. <input type="checkbox"/> A substitute specification. | | | | | |
| 16. <input type="checkbox"/> A change of power of attorney and/or address letter. | | | | | |
| 17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. | | | | | |
| 18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). | | | | | |
| 19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). | | | | | |
| 20. <input type="checkbox"/> Other items or information: | | | | | |

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| U.S. APPLICATION NO. 10/031220 INTERNATIONAL APPLICATION NO. PCT/CN00/00196 | | ATTORNEY'S DOCKET NUMBER 20291.US | |
| 21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. \$1040.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO. \$890.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO. \$740.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4). \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4). \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT = \$ 1040.00 | | CALCULATIONS PTO USE ONLY | |
| Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(e)). <input type="checkbox"/> 20 <input type="checkbox"/> 30 | | \$ | |
| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE |
| Total claims | 9 - 20 = | 0 | x \$18.00 |
| Independent claims | 1 - 3 = | 0 | x \$84.00 |
| MULTIPLE DEPENDENT CLAIM(S) (if applicable) | | + \$280.00 | |
| TOTAL OF ABOVE CALCULATIONS = | | \$ 1040.00 | |
| <input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. | | + \$ 520.00 | |
| SUBTOTAL = | | \$ 520.00 | |
| Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492(f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30 | | \$ 00 | |
| TOTAL NATIONAL FEE = | | \$ 520.00 | |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property + | | \$ | |
| TOTAL FEES ENCLOSED = | | \$ 520.00 | |
| | | Amount to be refunded: | \$ |
| | | charged: | \$ |
| a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>520.00</u> to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>20-0100</u> A duplicate copy of this sheet is enclosed. d. <input type="checkbox"/> Fees are to be charged to a credit card. WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038. | | | |
| NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status. | | | |
| SEND ALL CORRESPONDENCE TO: M. Wayne Western THORPE NORTH & WESTERN, LLP 8180 South 700 East, Ste. 200 Sandy, UT 84070 | | | |
| | | SIGNATURE | M. Wayne Western NAME |
| | | 22,788 REGISTRATION NUMBER | |
| Express Label No. EL580061490US | | | |

1/PRTS

WO 01/05908

PCT/CN00/00196

A PROCESS FOR PRODUCING GASOLINE AND DIESEL FROM
WASTE PLASTICS AND/OR HEAVY OIL

Field of the Invention

- 5 The present invention relates to a process for producing low-boiling point hydrocarbons from waste plastics and/or heavy oil, and more particularly to a process for producing gasoline and diesel through pyrolysis and catalytic cracking of waste plastics and/or heavy oil.

10 Background of the Invention

- Many methods for preparing low-boiling hydrocarbons from waste plastics and high-boiling hydrocarbons are known. U.S. Patent No. 4,851,601 and EP-A-0607862 (Applicant: MAZDA MOTOR CORPORATION) disclose a reaction of pyrolysis in a reactor kettle
- 15 (vertical or horizontal), wherein the outside wall of the kettle is heated at a high temperature while the materials therein are heated indirectly.

- In this method, the outside wall is apt to be deformed when the reactor is heated directly at a high temperature. The materials are readily sintered on the inside wall because of local over-heating so that the
- 20 conversion yield of the reaction and the life of the reactor are greatly decreased. In addition, the coefficient of the reactor's heat transfer is relatively low, it is difficult to drain the reaction residues, and the

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catalytic reaction in the fixed bed needs a separate heat supply. These are the common drawbacks of the reactor kettle in the prior art.

A spiral reactor utilized in some special fields is similar to the above. Heat is indirectly transferred when it works. The outside wall of the reactor is heated directly at a very high temperature, making the materials in the reactor indirectly heated. Therefore, the heat transfer coefficient is not satisfactory. Particularly, because the screw therein is apt to be deformed at a high temperature, making it hard to seal the two ends of the screw so that gas generated in the reaction may be exhausted.

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Summary of the Invention

Accordingly, an object of the invention is to provide a process for producing gasoline and diesel from waste plastics and/or heavy oil (including high-boiling hydrocarbons) to overcome the shortcomings in the prior art as described above.

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The process of the present invention comprises the steps of:

- (a) mixing waste plastics and/or heavy oil with a first catalyst at a high temperature in a pyrolysis reactor to carry out a reaction of pyrolysis and first catalytic cracking simultaneously; and
- (b) introducing the products in step (a) into a fixed bed to perform a reaction of second catalytic cracking.

20

Said first catalyst is made as follows: powder Al_2O_3 is mixed with water glass to obtain a slurry, and the resultant slurry is then mixed with catalyst HZSM-5. The resultant mixture is dried, formed, granulated, and heated to obtain the first catalyst.

- 5 The ratio between powder Al_2O_3 and water glass is 1:3-5 by weight and that between the slurry and HZSM-5 is 1:0.2-0.5 by weight.

According to the process of the invention, the materials can be converted to gasoline and diesel with a high yield, and the requirements for the reactor are not strictly defined because the first catalyst is used to
10 heat the materials directly.

Brief Description of the Drawing

Figure 1 is an operational flow chart of the process in the invention.

15 Detailed Description of the Invention

The process of the present invention comprises the steps of:

- (a) mixing waste plastics and/or heavy oil with a first catalyst at a high temperature in a pyrolysis reactor to carry out a reaction of pyrolysis and first catalytic cracking simultaneously; and
20 (b) introducing the products in step (a) into a fixed bed to perform a reaction of second catalytic cracking.

The process of the invention further comprises a step of:

(c) recycling the first catalyst in the reaction.

The reaction of pyrolysis and first catalytic cracking may be conducted under the standard atmosphere or higher, and the temperature of the first catalyst may be controlled at 500-1,000°C, preferably 600-
5 700°C.

The reaction of second catalytic cracking is carried out with a second catalyst in the fixed bed at 300-600°C, preferably 300-450°C.

The second catalyst used in the invention may be the commonly used catalyst in the reaction of catalytic cracking in the art.

10 In the invention, the first catalyst after being heated to a high temperature in the combustion chamber the first catalyst is charged into a pyrolysis reactor by using a spiral conveyor. Waste plastics (or heavy oil) are charged into the sealed pyrolysis reactor, and there they are directly mixed with the hot first catalyst to perform a reaction of pyrolysis and
15 first catalytic cracking. The materials are decomposed into gaseous hydrocarbons and residues. The gaseous hydrocarbons then enter a fixed bed in the reactor and are further decomposed into smaller molecules via a second catalytic cracking. Gaseous substances from the reaction are collected by means of the conventional process in the prior art so as to
20 obtain gasoline and diesel. Said first catalyst and residues in the reaction are introduced into a gasification chamber by a screw, and further into a separator by a spiral conveyor. Hot flue gas is led into the separator

with a blower, which blows said mixture into a cyclone separator so as to collect a solid mixture. Said mixture is introduced into a combustion chamber by a spiral conveyor. In the combustion chamber, organic substances in the mixture are burnt out, while the first catalyst is heated
5 and delivered to the spiral reactor again.

In the above-mentioned process, the feedstock is mixed directly with hot first catalyst, and pyrolysis and the first catalytic cracking take place at the same time. The first catalyst is not only used as a heating medium but also as a catalyst, which can be recycled.

10 Said first catalyst is made as follows: powder Al_2O_3 is mixed with water glass to obtain a slurry, and the resultant slurry is then mixed with catalyst HZSM-5; and the resultant mixture is dried, formed, granulated, and heated at a temperature of 550-800°C. The ratio between powder Al_2O_3 and water glass to be used is 1:3-5 by weight and that between the
15 slurry and HZSM-5 is 1:0.2-0.5 by weight. Said first catalyst used in the invention is generally of a Mohs' scale of hardness of 7-9 and a diameter of 0.2-0.5mm.

In the above process, said pyrolysis and first catalytic cracking may be conducted under standard atmosphere or higher. The reaction
20 temperature, when the first catalyst is transmitted from the combustion chamber to the pyrolysis reactor, is controlled at 500-1000°C, preferably 600-700°C. The temperature of the first catalyst is kept at 400-800°C,

preferably 500-600°C when it leaves the pyrolysis reactor.

Said second catalytic cracking is carried out in the fixed bed inside the gasification chamber. Heat required in the second catalytic cracking is provided by the gasification chamber itself. The second catalytic reaction is undertaken at 230-600°C, preferably 300-450°C. A particular catalyst DL-1 being composed of (Wt. %): 8% of CHO-1(a commodity produced by China Qilu Petrochemical Factory), 24% of REY, 25% of flokite (silicon/aluminum =12/1) and 43% of catalyst ZSM-5 is used in the second catalytic cracking after being thoroughly mixed and calcined.

The present invention will be more distinct with reference to the accompanying drawings.

Referring to Fig. 1, a first catalyst 16 in the granular form is charged into a combustion chamber 21 from a storage tank 26 with a spiral conveyor 27. Fuel oil (or recuperated pyrolysis gas) and air are sprayed into the combustion chamber 21 simultaneously via nozzles 18, 19 and 20. The first catalyst 16 in the combustion chamber 21 is heated to 500-1,000°C and subsequently led into a storage tank 17. A spiral conveyor 29 is started by a motor 1 to push the first catalyst 16 continuously into a pyrolysis reactor 14. At the same time, the materials to be treated are pushed by a screw (or reciprocating) extruder 4 into a spiral reactor 14. If the materials are heavy oils, they may be pumped into the sealed

pyrolysis reactor 14 via an inlet 28. The materials are mixed directly with the first catalyst 16 in the reactor 14 to undergo a pyrolytic reaction and a first catalytic cracking. Rotated and pushed by the spiral conveyor 2, gaseous hydrocarbons generated from the reaction and residues move forward to enter a vaporizer 13. Gaseous hydrocarbons enter a fixed bed 12 in the vaporizer 13 through the vaporization region, and react with a second catalyst to generate gaseous hydrocarbons with small molecules, which will be fractionated in a fractional column 9 to obtain gasoline and diesel by means of the conventional process. A mixture 10 of reaction residues and the first catalyst 16 entering the bottom of the vaporizer 13 is driven into a separator 8 via a spiral conveyor 2. A blower 3 is employed to push the high-temperature flue gas into the separator 8 via an entrance 6. Solid mixture 25 containing the first catalyst are flown up to enter a cyclone 24 because they are lighter. Other heavy residues enter the bottom of the separator 8 and are discharged from a hole 7. Thus, the solid mixture 25 in the cyclone 24 drops into a storage tank 26, and then is charged into the combustion chamber 21 by the spiral conveyor 27. In the combustion chamber 21, organic substances in the mixture 25 are burnt out and inorganic dusts are extracted together with high-temperature flue gas. The first catalyst 16 is hereby recovered and falls into the storage tank 17, subsequently. The heated first catalyst is then charged into the reactor 14 by the spiral conveyor 29.

The invention is further described by the following examples.

Example 1

- 5 Water glass (1,600kg, modulus>3) and powder Al_2O_3 (400kg) were completely mixed to obtain a slurry. The slurry was mixed with catalyst HZSM-5 (800kg). The resultant mixture was dried, formed, granulated, and heated at 800°C for 4 hours to obtain the first catalyst with a Mohs' scale of hardness of 8.5 and a diameter of 0.4 mm.
- 10 2,000 kg of the first catalyst prepared as indicated above was charged into the combustion chamber 21, and simultaneously sprays 0# diesel (or recuperated pyrolysis gas) and air were led into the combustion chamber 21 to burn. The first catalyst was heated up to 600-700°C and then led into the pyrolysis reactor 14. The screw (or reciprocating) extruder 4 was
- 15 used to push 1,400kg of waste plastics (PP25%, PS25%, and PE50%) into the reactor 14 to perform the reaction. The temperature at the stock inlet of the reactor 14 was controlled at 600-700°C, whereas the temperature at the residue outlet thereof was controlled at 500-600°C. The catalyst DL-1 was arranged in the fixed bed 12, and the second catalytic reaction was
- 20 conducted therein. The reaction pressure was kept at 0.05-0.1 MPa. Gasoline and diesel were obtained from the fractional column 9. The mixture of the first catalyst and residues was charged into the combustion

chamber 21 and was heated up to 600-700°C therein to separate the first catalyst. The recovered first catalyst was introduced into the reactor 14 for heat supply.

5 Products generated from this Example are listed below:

1. Gasoline, 630kg, RON=93.5, components (by wt%): paraffin 19.9%,
cyclanes 12%, olefin 48%, arenes 9.9%, others 10.2%;
2. Diesel, 420kg, cetane value=52, components (by wt%): paraffin
15%, cyclanes 8%, olefin 55%, arenes 10%, others 12%;
- 10 3. Inorganic residues 140kg;
4. Flammable gas 210kg.

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What I claim is:

1. A process for producing gasoline and diesel from waste plastic and/or heavy oil comprises the steps of:

5 (a) mixing waste plastic and/or heavy oil with a first catalyst in a pyrolysis reactor at high temperature to carry out a pyrolytic reaction and a first catalytic cracking ; and

(b) introducing the products in step (a) into a fixed bed to perform a second catalytic cracking with a second catalyst.

10 2. A process as claimed in Claim 1, wherein said first catalyst is made as follows: powder Al_2O_3 is mixed with water glass to obtain a slurry, and the resultant slurry is then mixed with catalyst HZSM-5; and resultant mixture is dried, formed, granulized, and heated at 550-800°C.

3. A process as claimed in Claim 2, wherein the ratio between powder
15 Al_2O_3 and water glass is 1:3-5 by weight and that between the slurry and HZSM-5 is 1:0.2-0.5 by weight.

4. A process as claimed in Claim 3, wherein said first catalyst is of a Mohs' scale of hardness of 7-9, and a diameter of 0.2-0.5mm.

5. A process as claimed in Claim 1, wherein the process further comprises
20 the step of:

c) recycling the first catalyst in the reaction.

6. A process as claimed in Claim 1, wherein said catalyst in the fixed bed

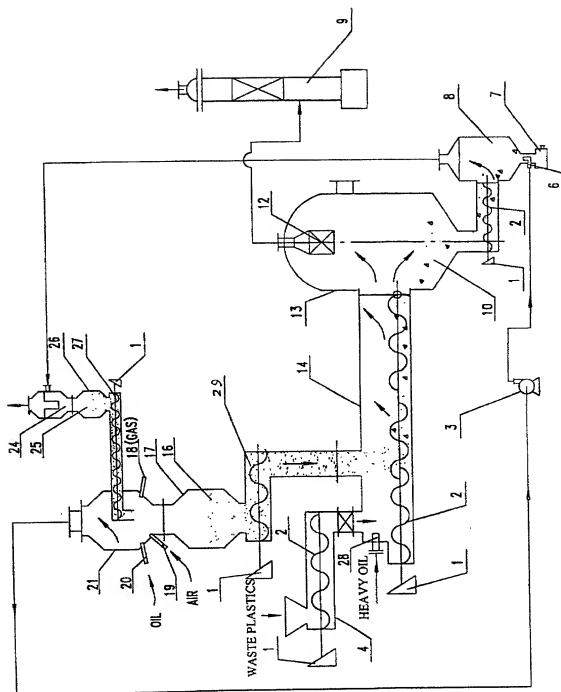
comprises 8% of CHO-1, 24% of REY, 25% of flokrite and 43% of catalyst ZSM-5, by weight.

7. A process as claimed in Claim 1, wherein the process is performed under the standard atmosphere or higher.

5 8. A process as claimed in Claim 1, wherein the temperature of the first catalyst is controlled at 500-1,000°C before entering the pyrolysis reactor, and is controlled at 400-800°C while leaving the pyrolysis reactor.

9. A process as claimed in Claim 1, wherein the first catalyst advances in the same flow direction as that of the waste plastics and/or heavy oil.

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PATENT APPLICATION
ATTORNEY DOCKET NO 2029 US

DECLARATION AND PETITION

As a below named inventor, I hereby declare: that my residence, post office address, and citizenship are as stated below next to my name; that I verily believe I am the original, first, and sole inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled A PROCESS FOR PRODUCING GASOLINE AND DIESEL FROM WASTE PLASTICS AND/OR HEAVY OIL, the specification of which is attached hereto; that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment specifically referred to above; and that I acknowledge the duty to disclose information which is material to patentability as defined in § 1.56(a) of Title 37 of the Code of Federal Regulations.

I hereby claim the benefit under Section 119 of Title 35 of the United States Code of the earlier filed patent application filed with the World Intellectual Property Organization as application no. PCT/CN00/00196, WO01/05908 filed on July 13, 2000; and, insofar as the subject matter of each of the claims of these applications is not disclosed in the earlier filed pending applications in the manner provided by the first paragraph of Section 112 of Title 35 of the United States code, we acknowledge the duty to disclose material information, as defined in Section 1.56(a) of Title 37 of the Code of Federal Regulations, which occurred between the filing date of the earlier filed applications and the filing date of this application.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful, false statements and the like so made are punishable by

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fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code, and that such willful, false statements may jeopardize the validity of the application or any patent issuing thereon.

Wherefore, I pray that Letters Patent be granted to me for the invention or discovery described and claimed in the foregoing specification and claims, declaration, and this petition.

Signed at Beijing, China, this 16 day of Jan, 2002.

INVENTOR:

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